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New rhodium–ruthenium heterobimetallic complexes with bridging bi- or tri-dentate phosphine ligands

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Abstract

The mononuclear chelated complex [RuCl(Cp)(η^2-dppa)] has been synthesised and reacted with [$Rh_2Cl_2(CO)_4$] to form the heterobimetallic complex [(Cp)Ru(μ-CO)$_2${(μ-$Ph_2PN(H)PPh_2$}$RhCl_2$]. Complexes of [RuCl(Cp){$(PPh_2)_2CHCH_2PPh_2$}] have been reacted with [$Rh_2Cl_2(CO)_4$] or [RhCl$(CO)_2$(*p*-toluidene)]. Characterisation of these new ruthenium complexes was carried out using ^{31}P-NMR, FAB mass spectroscopy, elemental analysis and IR spectrophotometry. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Rhodium; Heterometallic complexes; Tridentate phosphines; Bidentate phosphines

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1. Introduction

The use of bidentate phosphine ligands, especially bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$ (dppe), bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$ (dppm), and bis(diphenylphosphino)ethene, $Ph_2PC(=CH_2)PPh_2$ (dppen), has become increasingly frequent [1–4]. The versatility of dppe, dppm and dppen arises from their ready coordination to metal centres through the lone pair of electrons at one or both of the phosphorus atoms. Compared with the vast body of data accumulated on diphosphines in which the phosphorus nuclei are linked by a carbon atom or chain, less has appeared on ligands where the backbone of the molecule comprises a heteroatom or group. In this respect bis(diphenylphosphino)amine, $Ph_2PN(H)PPh_2$ (dppa), has received our attention because dppe, dppm or dppen and dppa have shared features in the formation of bimetallic complexes. We have previously reported the ring-opening reaction of [RuCl(Cp)(η^2-dppen)] with [$Rh_2Cl_2(CO)_4$], which leads to the formation of the heterobimetallic complex [(Cp)Ru(μ-CO)$_2${μ-$Ph_2PC(=CH_2)PPh_2$}$RhCl_2$] [3]. We have therefore employed this reaction to synthesise [RuCl(Cp)(η^2-dppa)] **1** and then investigated the extent and potential of ring-opening reaction to synthesise heterobimetallic Ru–Rh complexes. It has been reported that a Michael-type addition occurs across the double bond of dppen. This addition reaction occurs both on the uncomplexed dppen [5] and, more readily, on complexed dppen [6]. We have therefore employed this reaction to synthesise [RuCl(Cp){$(PPh_2)_2CHCH_2PPh_2$}] [7] and made use of the dangling phosphine created in this way to synthesise heterobimetallic complexes. This paper reports the results of the treatment of [RuCl(Cp)(η^2-dppa)] and [RuCl(Cp){$(PPh_2)_2CHCH_2PPh_2$}] with [$Rh_2Cl_2(CO)_4$].

2. Results and discussion

The compound $Ph_2PN(H)PPh_2$ (dppa) was prepared by treatment of a diethylether solution of $(Me_3Si)_2NH$ with Ph_2PCl [8]. It was characterised by elemental analyses (C-, H- and N-) and NMR spectroscopy. The ^{31}P-NMR spectrum shows a single peak at δ +43.1. There is a progressive shift upfield, therefore, from dppm (δ −22.1) to dppen (δ −3.1) to dppa.

Treatment of [RuCl(Cp)$(PPh_3)_2$] in toluene with one equivalent of dppa gave an orange complex, microanalytical data for which were consistent with the formula

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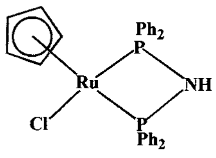
[RuCl(Cp)(η^2-dppa)] **1**. The ^{31}P-NMR spectrum of **1** shows a single sharp peak at δ +71.95 due to the equivalence of the coordinated phosphine groups.

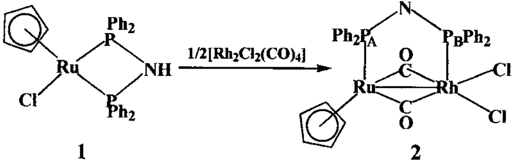


1

Analysis by FAB mass spectroscopy gave the molecular ion at the desired position, $m/z = 587$. The next significant peak appears at $m/z = 552$, indicating a loss of 35 amu. This suggests the loss of chlorine from the ruthenium centre. An impurity peak at $m/z = 814$ was observed; this is suggested to be due to the loss of chlorine from the singly substituted molecule [RuCl(Cp)PPh$_3$(dppa-*p*)] **2**, although there was no ^{31}P-NMR evidence for this complex.

On treatment of [RuCl(Cp)(η^2-dppa)] **1** with 0.5 equivalent of [Rh$_2$Cl$_2$(CO)$_4$] in dichloromethane, the yellow heterobimetallic product [(Cp)Ru(μ-CO)$_2${(μ-Ph$_2$PN(H)PPh$_2$}RhCl$_2$] **2** is formed as shown in Fig. 1. This preparation involves the ring-opening reaction of [RuCl(Cp)(η^2-dppa)] with [Rh$_2$Cl$_2$(CO)$_4$]. This is a common preparative route for the synthesis of ligand-bridged heterobimetallics and similar reactions have been carried out successfully using [RuCl(Cp)(η^2-dppen)] [6] and [RuCl(Cp)(η^2-dppm)] [9].

The heterobimetallic complex **2** has been confirmed by the microanalytical data and the presence of bridging carbonyl in the infrared spectrum (ν(CO) 1825 cm^{-1}) and, further, by the fact that the ^{31}P-NMR spectrum shows a doublet and a doublet of doublets. This pattern arises from two different phosphorus atoms, P_A and P_B. The doublet at 102.3 ppm is formed by coupling of P_A–P_B, with a coupling constant (J_{PP} of 70 Hz, consistent with the analogous dppm bridged bimetallic complex. The doublet of doublets at δ 85.2 is formed by coupling of P_B–P_A to form a doublet, then further coupling of P_B to rhodium giving a doublet of doublets with coupling constants $^2J_{PP} = 70$ Hz and $^1J_{PRh}$ 128 Hz, both are consistent with the dppm bridged bimetallic. Analysis by FAB mass spectroscopy of the heterobimetallic complex **2** did not gave a molecular ion peak at the desired position of $m/z = 781$. A peak at $m/z = 746$, however, was observed. There is a difference of 35 amu, indicating the loss of chlorine as seen for the previous complex **1**. The spectrum also shows a peak at $m/z = 690$, a difference of 56 amu, corresponding to the loss of the two bridging carbonyl groups. As with the complex **1** an impurity peak at $m/z = 814$ was observed due to [RuCl(Cp)PPh$_3$(dppa-*p*)] complex. No reaction had occurred between [RuCl(Cp)PPh$_3$(dppa-*p*)] and [Rh$_2$Cl$_2$(CO)$_4$]. This is probably due to the fact that [RuCl(Cp)PPh$_3$(dppa-*p*)] complex has no chelate ring and, therefore, is less likely to undergo the metal insertion reaction. Elemental analysis of [(Cp)Ru(μ-CO)$_2${(μ-Ph$_2$PN(H)PPh$_2$}RhCl$_2$] complex **2** shows good agreement between theoretical and obtained values. The infrared spectrum shows a single metal–carbonyl band in the bridging region (1825 cm^{-1}) and a strong band at 300 cm^{-1} due to Rh–Cl bond. A crystallisation was set up as with complex **1**. A suitable yellow crystal was selected and mounted in a Lindemann tube. However, as data collection proceeded the crystal lost solvent, rendering it useless for X-ray purposes.



1 **2**

Fig. 1.

A Michael-type addition of the N–H bond of [RuCl(Cp)(η^2-dppa)] across both coordinated and uncoordinated dppen was examined. The results for uncoordinated dppen showed no reaction had occurred. Reaction occurred with coordinated dppen but analysis of the products gave inconclusive results.

The complex [RuCl(Cp)(η^2-dppen)] **3** was prepared in high yield by treatment of [RuCl(Cp)(PPh$_3$)$_2$] with dppen [3]. The complex [RuCl(Cp){(PPh$_2$)$_2$CHCH$_2$-PPh$_2$}] **4**, is formed in quantitative yield by the base (KOBu^t)-catalysed addition of diphenylphosphine to [RuCl(Cp)(η^2-dppen)] solution in tetrahydrofuran [4]. The presence of a dangling phosphine in complex **4** provides an opportunity for further reactions with different metal centres. The treatment of the uncoordinated phosphine group of complex **4** with [Rh$_2$Cl$_2$-(CO)$_4$] in THF at ambient temperature gave an unstable heterobimetallic [RuCl(Cp){(PPh$_2$)$_2$CHCH$_2$-PPh$_2$}Rh(CO)$_2$Cl] **5**, characterised on the basis of its infrared spectrum and by ^{31}P-NMR spectroscopy and microanalysis. The infrared spectrum of complex **5** shows bands due to the LRh(CO)$_2$Cl [10] moiety at 2078, 2010 and 1975 cm^{-1}. The ^{31}P-NMR spectrum of complex **5** shows a resonance at δ 41.5 ppm (t, J_{PP} 2.44) due to two phosphorus atoms coordinated to Ru, and a resonance centred at δ 22.1 ppm (d of t, J_{PRh} 125.7, J_{PP} 2.44 Hz) due to the phosphorus atom coordinated to Rh, in the ratio 2:1, as expected (Table 1). Complex **5** transforms slowly in solution over a period of 48 h, or immediately on addition of Me$_3$NO, into $[(Cp)Cl\{\overline{Ru(PPh_2)_2CHCH_2PPh_2Rh}(CO)_2Cl]$ complex **6**. Again, this complex has been characterised by spectroscopic methods. The infrared spectrum of complex **6** shows two CO bands due to the LRh(CO)$_2$Cl moiety,

Table 1
Spectroscopic data

Compound	^{31}P-NMR [a]	IR (cm^{-1}) [b]
[RuCl(Cp)(η^2-dppa)] **1**	71.95 [s]	–
[(Cp)Ru(μ-CO)$_2${(μ-Ph$_2$PN(H)PPh$_2$}RhCl$_2$] **2**	102.3 [d, J_{PP} 70], 85.2 [dd, J_{PP} 70; J_{PRh} 128]	2140, 2108, 2040, 1985, 1825
[RuCl(Cp)(η^2-dppen)] **3**	31.77 [s]	–
[RuCl(Cp){(PPh$_2$)$_2$CHCH$_2$PPh$_2$}] **4**	36.8 [d, J_{PP} 9.8, P$_A$], −22.0 [t, P$_X$]	–
[RuCl(Cp){(PPh$_2$)$_2$CHCH$_2$PPh$_2$}Rh(CO)$_2$Cl] **5**	41.5 [d, J_{PP} 2.44], 22.1 [d of t, J_{PP} 2.44; J_{PRh} 125.7]	2078, 2010, 1975
[(Cp)Cl{Ru(PPh$_2$)$_2$CHCH$_2$PPh$_2$Rh(CO)$_2$Cl}] **6**	39.8 [d, J_{PP} 9.8], 26.2 [d of t, J_{PP} 9.8; J_{PRh} 111.1]	2023, 1962

[a] In THF/C$_6$D$_6$; coupling constants in Hz; P$_A$ refers to two equivalent P atoms bound to Ru, P$_X$ refers to the unique P atom.
[b] ν(CO), in CH$_2$Cl$_2$.

(2023, 1962 cm^{-1}). The ^{31}P-NMR spectrum is identical to that obtained for [{(CO)$_3$Fe(Ph$_2$P)$_2$CHCH$_2$PPh$_2$Rh-(CO)$_2$Cl}] [11]. It shows a resonance at δ 39.8 ppm due to two phosphorus atoms coordinated to Ru, and a resonance centred at δ 26.2 ppm (d of t, J_{PRh} 111.1, J_{PP} 9.8 Hz) due to the phosphorus atom coordinated to Rh. The high-frequency νCO band (at ca. 2023 cm^{-1}) in the infrared spectrum of Ru–Rh complex, and the phosphorus–phosphorus coupling constant of 9.8 Hz similar to that of [(CO)$_3$Fe{(PPh$_2$)$_2$CHCH$_2$PPh$_2$Rh-(CO)$_2$Cl}] [11], and larger than that of [(CO)$_3$-Fe{(PPh$_2$)$_2$CHCH$_2$PPh$_2$Rh(CO)$_3$Cl$_2$}] [12] suggest that a donor Ru→Rh bond is present (Scheme 1). The uncoordiated phosphine group of complex **4** also reacts with [RhCl(CO)$_2$(p-toluidene)] to give the hetero-bimetallic complex **5**. The infrared spectrum of this complex and ^{31}P-NMR spectrum is typically identical to that previously described for complex **5**, suggesting that the tppe ligand ((PPh$_2$)$_2$CHCH$_2$PPh$_2$) bridges the Ru and Rh atoms, and p-toluidene has not remained coordinated to the rhodium. Again, the transformation of **5** to complex **6** occurred by addition of Me$_3$NO.

3. Experimental

All reactions were carried out under nitrogen unless otherwise stated, using dry, degassed solvents and standard Schlenk-line techniques. IR spectra were recorded as dichloromethane solutions in 0.5 mm NaCl cells on a Perkin–Elmer 681 spectrophotometer; NMR spectra were recorded on Jeol FX-60 or Bruker WM250 instruments. Chemical shifts are relative to 85% H$_3$PO$_4$ for ^{31}P-NMR spectra. Microanalyses were carried out in the Department of Chemistry, University of Liverpool. FAB atom bombardment mass spectroscopy was used to run all the samples in 3-nitrobenzyl alcohol for a duration of 16 min.

The compounds PPh$_2$N(H)PPh$_2$ [8], Ph$_2$PC(=CH$_2$)-PPh$_2$ [13], [RuCl(Cp)(η^2-dppen)] [3], [RuCl(Cp)(PPh$_3$)$_2$] [14], [RhCl(CO)$_2$(p-toluidene)] [15] and [Rh$_2$Cl$_2$(CO)$_4$] [16] were prepared according to published procedures.

3.1. Preparation of [RuCl(Cp)(η^2-dppa)] **1**

A solution of [RuCl(Cp)(PPh$_3$)$_2$] (0.2g, 0.28 mmol) in toluene (70 cm^3) was added to the dppa (0.11 g, 0.28 mmol) in toluene (30 cm^3) with stirring. The solution was refluxed for 4 h, giving a red–orange coloured solution. This was evaporated to dryness. The remaining solid was purified by adding heptane to dissolve the liberated PPh$_3$. The pure product was collected by filtration and dried in vacuo. The remaining solid was recrystallised from toluene to give complex **1** as an orange solid (0.11g, 67%). Anal. Found: C, 59.17; H, 4.64; N, 2.09%. RuC$_{29}$H$_{26}$NClP$_2$ requires C, 59.34; H, 4.46; N, 2.39%.

3.2. Preparation of [(Cp)Ru(μ-CO)$_2${(μ-Ph$_2$PN(H)-PPh$_2$}RhCl$_2$] **2**

[RuCl(Cp)(η^2-dppa)] (0.1 g, 0.17 mmol) and [Rh$_2$Cl$_2$(CO)$_4$] (0.033g, 0.09 mmol) were added to degassed dichloromethane (50 cm^3) in the strict absence of air. The reaction mixture was stirred for 1 h. The yellow product was collected by slowly blowing off the solvent (0.073 g, 54.8%). Anal. Found: C, 47.29; H, 3.39; N, 1.73%. RuRhC$_{31}$H$_{26}$NCl$_2$P$_2$O$_2$ requires C, 47.63; H, 3.36; N, 1.79%.

3.3. Preparation of [RuCl(Cp)(η^2-dppen)] **3**

A solution of [RuCl(Cp)(PPh$_3$)$_2$] (0.362 g, 0.48 mmol) and dppen (0.203 g, 0.52 mmol) in toluene (100 cm^3) was refluxed for 5 h. The volume of the solution was reduced to 15 cm^3 by evaporation under vacuum, and hexane (50 cm^3) was added. On standing for 24 h at −20°C, the solution gave dark red crystals of [RuCl(Cp)(η^2-dppen)] (0.24 g, 85%). Anal. Found: C, 62.0; H, 4.4%. RuC$_{31}$H$_{27}$ClP$_2$ requires C, 62.26; H, 4.55%; M$^+$ at m/z 598. M$^+$ based on ^{101}Ru and ^{35}Cl, 598.

3.4. Reaction of [RuCl(Cp)(η^2-dppa)] with dppen

A solution of [RuCl(Cp)(η^2-dppa)] (0.06 g, 0.10 mmol) and dppen (0.04 g, 0.10 mmol) in toluene (100

cm^3) was stirred at room temperature (r.t.) until a colour change was observed. The volume of the solution was reduced to 15 cm^3 by evaporation under vacuum. Analysis was carried out by ^{31}P-NMR. This reaction failed as shown by ^{31}P-NMR. There was singlets at 71.95 and −3.1 ppm corresponding to [RuCl(Cp)(η^2-dppa)] and dppen, respectively.

3.5. Reaction of [RuCl(Cp)(η^2-dppa)] with [RuCl(Cp)(η^2-dppen)]

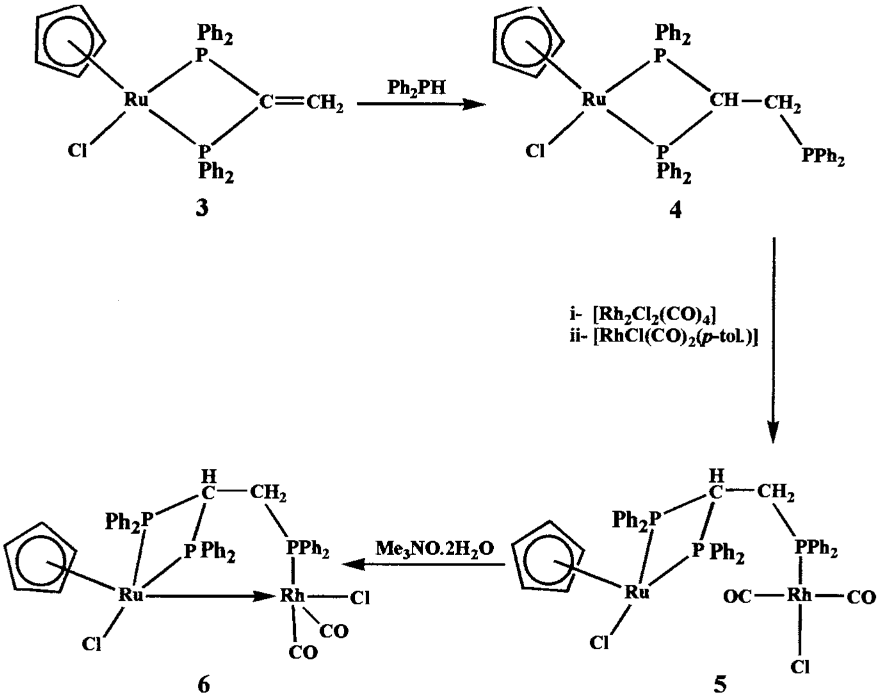
[RuCl(Cp)(η^2-dppa)] (0.1 g, 0.17 mmol) and [RuCl(Cp)(η^2-dppen)] (0.1 g, 0.17 mmol) were added to a flask containing degassed toluene (50 cm^3). A catalytic amount of potassium *tert*-butoxide (KOBu^t) was added and the reaction mixture was stirred overnight under a nitrogen atmosphere at r.t. The solvent was removed by evaporation under vacuum. Analysis of the product was carried out by ^{31}P-NMR. The reaction was showing several products with ^{31}P-NMR. These products were dissolved in chloroform and thin-layer chromatography (TLC) using 1:3 dichloromethane–acetone was carried out on the solution. The separation produced four bands ranging from brown to pale yellow. Unfortunately, extraction of these bands failed to give any products. It is assumed that the products had decomposed on the TLC plate.

3.6. Preparation of [RuCl(Cp){$(PPh_2)_2CHCH_2PPh_2$}-$Rh(CO)_2Cl$] **5**

The freshly prepared [RuCl(Cp){$(PPh_2)_2CHCH_2$-PPh_2}] (0.058 g, 0.074 mmol) in THF (10 cm^3) was stirred at r.t. with [$Rh_2Cl_2(CO)_4$] (0.019 g, 0.037 mmol) in THF. After 10 min, the solution was evaporated to dryness. The remaining solid was recrystallised from THF–benzene to give complex **5** as a yellow solid (0.059 g, 87.6%). Anal. Found: C, 55.28; H, 3.7%. $RuRhC_{45}H_{38}Cl_2P_3O_2$ requires C, 55.23; H, 3.91%.

3.7. [(Cp)Cl{$Ru(PPh_2)_2CHCH_2PPh_2Rh(CO)_2Cl$}] **6**

Complex **5** was dissolved in THF (10 cm^3) and stirred at 40°C for 48 h, after which time NMR spectroscopy showed reaction had occurred. $Me_3NO{\cdot}2H_2O$ (0.009 g, 0.074 mmol) in methanol (2 cm^3) was added to complex **5** dropwise and the mixture stirred at 40°C for 10 min. Spectroscopic analysis showed complete conversion to [(Cp)Cl{$Ru(PPh_2)_2CHCH_2PPh_2Rh(CO)_2Cl$}] complex **6** had occurred. The yellowish–brown solution was evaporated to dryness and the residue was recrystallised by slow evaporation from THF–benzene. Anal. Found: C, 54.9; H, 3.81%. $RuRhC_{45}H_{38}Cl_2P_3O_2$ requires C, 55.23; H, 3.91%.



Scheme 1.

3.8. Reaction of [RhCl(CO)$_2$(p-toluidene)] with [RuCl(Cp){(PPh$_2$)$_2$CHCH$_2$PPh$_2$}]

[RhCl(CO)$_2$(*p*-toluidene)] (0.0215 g, 0.0714 mmol) in THF (10 cm^3) was added to the yellow solution of [RuCl(Cp){(PPh$_2$)$_2$CHCH$_2$PPh$_2$}] (0.056 g, 0.0714 mmol), with stirring. Infrared monitoring confirmed complete reaction after stirring for 2 h at 50°C. The resulting yellowish–brown solution was evaporated to dryness and the yellow residue was recrystallised from THF–benzene to give complex **6** as a yellow solid (0.06 g, 53.6%). Anal. Found: C, 54.98; H, 3.8; 1.43%. $RuRhC_{45}H_{38}Cl_2P_3O_2$ requires C, 55.23; H, 3.91%.

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